

Communication

Can We Find an Optimal Fatty Acid Composition of Biodiesel in Order to Improve Oxidation Stability?

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Abstract: Air quality currently poses a major risk for human health. Currently, diesel is widely used as fuel and is a significant source of nitrogen oxides (NO_x) and particulate matter (PM), both hazardous to human health. A good alternative for mineral diesel is biodiesel, not only for the improvement of hazardous components in the exhaust gases but also because it can be produced in view of a circular economy. Biodiesel consists of a mix of different fatty acid methyl esters, which can react with oxygen. As a consequence, the oxidation stability of biodiesel has to be studied, because the oxidation of biodiesel could affect the performance of the engine due to the wear of injectors and fuel pumps. The oxidation stability could also affect the quality of the exhaust gases due to increases in NO_x and PM. The basic question we try to answer in this communication is: ‘Can we find an optimal fatty acid composition in order to have a maximal oxidation stability?’ In this article, we try to find the optimal fatty acid composition according to the five most common fatty acid methyl esters present in biodiesel in order to reach a maximal oxidation stability. The measurements and statistical analysis show, however, that there is no useful regression model because there are statistically significant two- and three-way interactions among the different fatty acids.

Keywords: fatty acid composition; biodiesel; oxidation stability; two- and three-way interactions



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1. Introduction

The use of mineral diesel nowadays poses two major problems: an increase in harmful pollutants, NO_x and particulate matter (PM), and in time, a decrease in the natural reserves needed to produce petroleum-based derivatives. Biodiesel is a good alternative, showing a lower production of harmful emissions, and it is a renewable source of combustible energy [1,2]. Although biodiesel shows these promising advantages, it shows an inferior oxidation stability compared to mineral diesel [2,3]. In this article, it is shown that the oxidation stability of biodiesel not only depends on the different fatty acid methyl esters (FAMES) themselves but also on the two- and three-way interactions among the different FAMES. There are different factors affecting the oxidation stability, such as UV radiation, humidity, temperature, the presence of metal in the fuel, and of course, the different types of methyl ester that determine the biodiesel. Biodiesel is produced using different types of raw vegetable oils, each with a specific mix of fatty acids. This mix changes with every plant oil used to commence production. Each fatty acid molecule has a different oxidation stability, and thus, the fatty acid composition plays a major role in the oxidation stability and the long-term storage of biodiesel. A major concern of the oxidation stability is a decrease in the burning characteristics and fuel filter blockage, and even the formation of carbon residue on fuel injectors [3].

Biodiesel oxidation shows in two types—auto-oxidation and photooxidation, where auto-oxidation seems to be the major cause of biodiesel oxidation. The auto-oxidative

degradation of biodiesel is a radical chain reaction and involves initiation, propagation, and termination steps. Photo-oxidation is a second type of biodiesel oxidation, but biodiesel is less affected by photo-oxidation. Auto-oxidation occurs when oxygen is present, whereas photo-oxidation also requires the presence of light [4].

The scope of our research was to find an optimal fatty acid composition of biodiesel with maximal oxidation stability. Adding antioxidants to biodiesel is a possibility, but looking at the composition might be another solution. The most common fatty acids found in vegetable oils are palmitic, stearic, oleic, linoleic, and linolenic acid [5]. This mix contains saturated, monounsaturated, and polyunsaturated fatty acids, and the saturation of the molecule is of major importance to the oxidation stability [6]. Polyunsaturated molecules are more susceptible to oxidation than monounsaturated [6–8]. This means each oil will have a different oxidation stability. Due to this fact, it may be that there is a fatty acid composition that will show a maximal oxidation stability. Regression analysis resulted in a final model with second- and third-order interaction terms, showing that the oxidation stability depended on complex interplay among different fatty acids.

2. Materials and Methods

Rapeseed methyl ester (RME, Bioro Biodiesel Refinery, Cargill Ghent, Belgium) was used as the biodiesel. Fatty acid methyl esters (purity > 95%) were purchased from TCI Chemicals, Zwijndrecht, Belgium, and Thermo Scientific, Geel, Belgium). These fatty acid methyl esters were added arbitrarily to change the composition. The exact compositions and oxidation times of different biodiesels were measured as follows.

The fatty acid profile was determined using a Thermo Scientific TRACE 1300 (Thermo Scientific, Geel, Belgium) equipped with a PTV injector (inlet temperature 250 °C) and an MS detector. Injections were performed using a PAL System autosampler (injection volume 1 µL). Chromeleon 7 software was used to control the system and to process the chromatograms and MS spectra. Measurements were performed on a RTX-2330 column from Restek (30 m × 0.25 mm × 0.20 µm). A constant flow of 1 mL helium/min was used in combination with the following temperature profile: 2 min at 70 °C, 13.5 °C/min to 180 °C, 5 min at 180 °C, and 6 °C/min to 240 °C. The MS parameters were set as follows: transfer line at 250 °C, ion source at 280 °C, electron ionisation, and a scan time of 0.2 s. Sample preparation included dilution of the sample in heptane and the addition of tetradecane (purity > 99%, Thermo Fischer) as an internal standard. The response factors of all the different fatty acid methyl esters were determined beforehand using a fatty acid methyl ester calibration mix containing 35 fatty acid methyl esters ranging from C4 to C24 (purchased from Sigma-Aldrich).

The oxidative stability was measured using an Oxitest apparatus from Velp Scientifica. Part of the sample (8 g) was put in a titanium sample holder and transferred to an oxidation chamber. Then, 6 bar of pure oxygen gas (99.999% purity) was applied, and the measurements were performed at 90 °C according to the procedure described in the AOCS standard procedure Cd-12c-16. The measurement resulted in an induction period, i.e., the time required to reach the starting point of oxidation.

The statistical method used was the modelling of the relation between the time until oxidation and the composition of the blend using multiple linear regression, with the time until oxidation as a dependent variable and the mass percentage of the fatty acids as an independent variable. Since these mass percentages are linearly dependent, adding up to 100%, one of the fatty acids had to be left out of the model to avoid multicollinearity. The model with four FAMES (when omitting one of them) resulted in acceptable variance inflation factors. The model was fitted using stepwise backward elimination, starting from a full factorial model with all three-way interactions. Among the different starting models (each of which omitting one FAME), we chose the one with the lowest VIF in the final model. The software used was R version 4.2.2 (<https://www.R-project.org/>; accessed on 1 December 2022) [9].

3. Results

3.1. Results of Measurements

We added the FAME showing double bonds to see if there was an influence on the oxidation stability. We also added a saturated FAME to see the influence of saturation. The goal, however, was looking for an optimal fatty acid composition. Tables 1–5 show the time needed for the complete oxidation of each of the blends, with the fatty acid as given. The oxidation times were measured for the blends after the addition of each of the main components of the biodiesel provided, with 1 mL, 2 mL, 3 mL, and 4 mL added to 10 mL of the biodiesel. In Table 1, the results are presented for the biodiesel with the added volumes of methyl stearate; Table 2 shows the added volumes of methyl linoleate; Table 3 shows those of methyl linolenate; and Table 4 shows those of methyl stearate. To obtain the data in Table 5, we added arbitrary volumes of arbitrary FAMES. The statistics of the measurements can be found in Supplementary Materials.

Table 1. Time needed for complete oxidation of rapeseed methyl ester biodiesel after addition of 1–4 mL pure methyl stearate (C18:1). Experiments were executed twice with each individual duration given for the specific composition of the biodiesel mixture.

| Added Volume (mL) | 1 | 2 | 3 | 4 |
|------------------------------|-------|-------|-------|-------|
| Palmitic acid, methyl ester | 3.68 | 3.91 | 4.14 | 4.22 |
| Stearic acid, methyl ester | 1.76 | 1.68 | 1.63 | 1.58 |
| Oleic acid, methyl ester | 53.77 | 54.72 | 55.06 | 56.23 |
| Linoleic acid, methyl ester | 28.00 | 27.98 | 27.13 | 27.02 |
| Linolenic acid, methyl ester | 12.79 | 11.71 | 12.03 | 10.96 |
| Time 1 (h:min) | 18:34 | 19:14 | 23:33 | 20:37 |
| Time 2 (h:min) | 18:54 | 19:02 | 23:03 | 21:03 |

Table 2. Time needed for complete oxidation of rapeseed methyl ester biodiesel after addition of 1–4 mL pure methyl linoleate (C18:2). Experiments were executed twice with each individual duration given for the specific composition of the biodiesel mixture.

| Added Volume (mL) | 1 | 2 | 3 | 4 |
|------------------------------|-------|-------|-------|-------|
| Palmitic acid, methyl ester | 2.99 | 3.39 | 2.98 | 2.85 |
| Stearic acid, methyl ester | 1.17 | 1.52 | 1.08 | 1.09 |
| Oleic acid, methyl ester | 49.82 | 42.48 | 40.52 | 37.59 |
| Linoleic acid, methyl ester | 35.51 | 40.33 | 46.09 | 48.87 |
| Linolenic acid, methyl ester | 10.50 | 12.29 | 9.33 | 9.61 |
| Time 1 (h:min) | 15:42 | 12:26 | 11:40 | 11:35 |
| Time 2 (h:min) | 15:55 | 12:27 | 11:35 | 11:30 |

Table 3. Time needed for complete oxidation of rapeseed methyl ester biodiesel after addition of 1–4 mL pure methyl linolenate (C18:3). Experiments were executed twice with each individual duration given for the specific composition of the biodiesel mixture.

| Added Volume (mL) | 1 | 2 | 3 | 4 |
|------------------------------|-------|-------|-------|-------|
| Palmitic acid, methyl ester | 3.58 | 3.49 | 3.36 | 3.12 |
| Stearic acid, methyl ester | 1.08 | 1.55 | 1.07 | 1.16 |
| Oleic acid, methyl ester | 46.64 | 38.76 | 37.01 | 32.58 |
| Linoleic acid, methyl ester | 24.89 | 23.13 | 21.53 | 21.53 |
| Linolenic acid, methyl ester | 23.81 | 33.06 | 37.04 | 41.61 |
| Time 1 (h:min) | 12:07 | 9:35 | 8:48 | 6:47 |
| Time 2 (h:min) | 12:36 | 9:50 | 9:00 | 6:21 |

Table 4. Time needed for complete oxidation of rapeseed methyl ester biodiesel after addition of 1–4 mL pure methyl palmitate (C16:0). Experiments were executed twice with each individual duration given for the specific composition of the biodiesel mixture.

| Added Volume (mL) | 1 | 2 | 3 | 4 |
|------------------------------|-------|-------|-------|-------|
| Palmitic acid, methyl ester | 11.95 | 19.60 | 24.61 | 29.45 |
| Stearic acid, methyl ester | 0.85 | 0.86 | 0.92 | 0.82 |
| Oleic acid, methyl ester | 51.40 | 46.31 | 44.72 | 40.38 |
| Linoleic acid, methyl ester | 24.76 | 22.22 | 21.31 | 19.12 |
| Linolenic acid, methyl ester | 11.04 | 11.01 | 8.45 | 10.23 |
| Time 1 (h:min) | 19:47 | 19:17 | 20:25 | 22:55 |
| Time 2 (h:min) | 19:50 | 19:12 | 19:56 | 24:25 |

Table 5. Time needed for complete oxidation of rapeseed methyl ester biodiesel after addition of arbitrary amounts of different FAMES (in mL). Each of the four experiments was executed twice with each individual duration given for the specific composition of the biodiesel mixture.

| Added Volume (mL) | 1 | 2 | 3 | 4 |
|------------------------------|-------|-------|-------|-------|
| Palmitic acid, methyl ester | 12.03 | 17.32 | 3.66 | 22.59 |
| Stearic acid, methyl ester | 1.02 | 0.96 | 1.47 | 1.31 |
| Oleic acid, methyl ester | 49.17 | 46.60 | 54.8 | 44.9 |
| Linoleic acid, methyl ester | 23.98 | 22.54 | 26.8 | 21.47 |
| Linolenic acid, methyl ester | 13.80 | 12.58 | 13.28 | 9.72 |
| Time 1 (h:min) | 19:57 | 22:34 | 16:37 | 24:21 |
| Time 2 (h:min) | 19:41 | 22:18 | 16:11 | 24:42 |

3.2. Data Analysis

Although it is possible to fit a (polynomial) regression model for each fatty acid methyl ester (FAME) separately, the FAMES in the blend interacted with one another—they changed each other's effect on the stability.

To model the effect of the FAME concentration on the oxidation stability, multiple linear regression models were fitted as described in the Methods section (Table 6). Due to the multicollinearity among the mass percentages of the five FAMES, one of the FAMES had to be omitted from the model. Among the various possible models, we chose the one that omitted the linolenic acid, as it had the lowest variance inflation factor in the resulting model. The variance inflation factor (VIF) was indeed unacceptably high when including all five FAMES in one model. Values over 5 are problematic, but here, these values were even much higher. Moreover, the variance inflation factors (VIF) when omitting the stearic methyl ester were also very high and we need to be cautious when interpreting these values.

Table 6. Variance inflation factors of each model when omitting none or one FAME.

| | All Included | No Palmitic | No Stearic | No Oleic | No Linoleic | No Linolenic |
|-----------|---------------|-------------|------------|----------|-------------|--------------|
| Palmitic | 1,791,465.754 | NA | 1520.192 | 5.058944 | 1.841572 | 2.163319 |
| Stearic | 2301.323 | 1.952844 | NA | 2.113770 | 2.022848 | 2.039071 |
| Oleic | 1,132,453.510 | 3.197950 | 1040.161 | NA | 2.172823 | 1.343666 |
| Linoleic | 1,669,835.968 | 1.716540 | 1467.775 | 3.203891 | NA | 1.437582 |
| Linolenic | 2,308,453.295 | 2.787618 | 2045.389 | 2.739000 | 1.987375 | NA |

NA: not applicable.

The next sets of models all omitted one of the FAMES (Table 7). Each time, a stepwise backward model was built, starting from a model with all the three-way interactions among the four FAMES. To describe how well the model predicted the outcome (time), the R^2 is given. The R^2 describes the variance (in oxidation time) explained by the regression model. More important here is that the root of the R^2 is the Pearson correlation (r) between the

observed time and the time predicted by the model. An R^2 value of 0.966 is extremely high, indicating that almost all of the variance in oxidation stability is explained by the variance in the FAME concentration. Conversely, this means that by using the FAME concentration, the oxidation stability can accurately be predicted.

Table 7. Different models for FAME interaction.

| Model without Linolenic Acid ($R^2 = 0.966$) | | | | |
|--|----------------------|------------------------|----------------|---------------------------|
| | Estimate | Std. Error | t Value | Pr(> t) |
| (Intercept) | 2.223×10^4 | 1.302×10^4 | 1.707 | 0.10013 |
| Palmitic | 1.068×10^3 | 3.848×10^2 | 2.776 | 0.01027 * |
| Stearic | -2.276×10^4 | 1.197×10^4 | -1.902 | 0.06879 |
| Oleic | -1.394×10^2 | 3.618×10^2 | -0.385 | 0.70328 |
| Linoleic | -1.672×10^3 | 5.895×10^2 | -2.837 | 0.00889 ** |
| Palmitic/stearic | -8.258×10^1 | 5.557×10^2 | -0.149 | 0.88306 |
| Palmitic/oleic | -1.491×10^2 | 5.894×10^1 | -2.531 | 0.01806 * |
| Palmitic/linoleic | 2.198×10^2 | 1.130×10^2 | 1.946 | 0.06301 |
| Stearic/oleic | 2.052×10^2 | 3.214×10^2 | 0.638 | 0.52902 |
| Stearic/linoleic | 1.599×10^3 | 5.459×10^2 | 2.929 | 0.00715 ** |
| Oleic/linoleic | 2.007×10^1 | 1.072×10^1 | 1.873 | 0.07281 |
| Palmitic/stearic/oleic | 1.110×10^2 | 4.794×10^1 | 2.316 | 0.02908 * |
| Palmitic/stearic/linoleic | -2.291×10^2 | 1.074×10^2 | -2.132 | 0.04299 * |
| Palmitic/oleic/linoleic | 1.000×10^0 | 3.554×10^{-1} | 2.815 | 0.00938 ** |
| Stearic/oleic/linoleic | -2.052×10^1 | 9.611×10^0 | -2.135 | 0.04273 * |
| Model without linolenic acid ($R^2 = 0.971$) | | | | |
| | Estimate | Std. Error | t value | Pr(> t) |
| (Intercept) | -1.566×10^4 | 4.431×10^3 | -3.534 | 0.001620 ** |
| Palmitic | 1.563×10^3 | 4.352×10^2 | 3.591 | 0.001404 ** |
| Stearic | 1.757×10^4 | 4.445×10^3 | 3.952 | 0.000560 *** |
| Oleic | 4.258×10^2 | 1.157×10^2 | 3.679 | 0.001125 ** |
| Linolenic | 3.912×10^2 | 2.199×10^2 | 1.779 | 0.087356 |
| Palmitic/stearic | -2.653×10^3 | 5.716×10^2 | -4.642 | 9.42×10^{-5} *** |
| Palmitic/oleic | -4.181×10^1 | 1.260×10^1 | -3.319 | 0.002774 ** |
| Palmitic/linolenic | 9.820×10^1 | 3.156×10^1 | 3.111 | 0.004617 ** |
| Stearic/oleic | -4.458×10^2 | 1.148×10^2 | -3.884 | 0.000667 *** |
| Stearic/linolenic | -5.229×10^2 | 1.893×10^2 | -2.762 | 0.010618 * |
| Oleic/linolenic | -1.361×10^1 | 6.233×10^0 | -2.184 | 0.038567 * |
| Palmitic/stearic/oleic | 6.655×10^1 | 1.491×10^1 | 4.463 | 0.000150 *** |
| Palmitic/stearic/linolenic | -2.910×10^1 | 2.290×10^1 | -1.271 | 0.215586 |
| Palmitic/oleic/linolenic | -1.538×10^0 | 6.925×10^{-1} | -2.221 | 0.035610 * |
| Stearic/oleic/linolenic | 1.609×10^1 | 5.355×10^0 | 3.004 | 0.005975 ** |
| Model without palmitic ($R^2=0.9467$) | | | | |
| | Estimate | Std. Error | t value | Pr(> t) |
| (Intercept) | 25,356.237 | 6422.679 | 3.948 | 0.000441 *** |
| Stearic | -22,626.241 | 5941.071 | -3.808 | 0.000645 *** |
| Oleic | -573.147 | 153.540 | -3.733 | 0.000791 *** |
| Linoleic | -933.565 | 247.288 | -3.775 | 0.000705 *** |
| Linolenic | 49.501 | 35.715 | 1.386 | 0.175970 |
| Stearic/oleic | 541.414 | 140.377 | 3.857 | 0.000565 *** |
| Stearic/linoleic | 875.116 | 227.005 | 3.855 | 0.000568 *** |
| Oleic/linoleic | 22.241 | 5.903 | 3.768 | 0.000720 *** |
| Linoleic/linolenic | -3.506 | 1.577 | -2.223 | 0.033918 * |
| Stearic/oleic/linoleic | -20.655 | 5.331 | -3.874 | 0.000539 *** |

Table 7. Cont.

| Model without oleic acid ($R^2 = 0.9565$) | | | | |
|---|-----------------|-------------------|----------------|--------------------|
| | Estimate | Std. Error | t value | Pr(> t) |
| (Intercept) | −565.334 | 1269.029 | −0.445 | 0.6594 |
| Palmitic | 469.404 | 314.066 | 1.495 | 0.1462 |
| Stearic | 5198.147 | 2033.371 | 2.556 | 0.0163 * |
| Linoleic | 100.172 | 53.884 | 1.859 | 0.0736 |
| Linolenic | −248.915 | 146.198 | −1.703 | 0.0997 |
| Palmitic/stearic | −1403.971 | 538.421 | −2.608 | 0.0145 * |
| Palmitic/linoleic | −24.038 | 14.267 | −1.685 | 0.1031 |
| Palmitic/linolenic | 71.410 | 39.602 | 1.803 | 0.0821 |
| Stearic/linoleic | −245.395 | 95.396 | −2.572 | 0.0157 * |
| Linoleic/linolenic | 10.005 | 6.824 | 1.466 | 0.1538 |
| Palmitic/stearic/linoleic | 66.577 | 25.101 | 2.652 | 0.0130 * |
| Palmitic/linoleic/linolenic | −3.196 | 1.827 | −1.749 | 0.0912 |
| Model without stearic ($R^2 = 0.948$) * | | | | |
| | Estimate | Std. Error | t value | Pr(> t) |
| (Intercept) | 53,900.1157 | 16,041.7195 | 3.360 | 0.00242 ** |
| Palmitic | 403.8778 | 434.2566 | 0.930 | 0.36090 |
| Oleic | −455.9423 | 160.4438 | −2.842 | 0.00861 ** |
| Linoleic | −1521.0857 | 595.2059 | −2.556 | 0.01680 * |
| Linolenic | −1575.3626 | 653.7127- | 0.930 | 0.02333 * |
| Palmitic/oleic | −98.6665 | 46.4231 | −2.125 | 0.04322 * |
| Palmitic/linoleic | 167.8947 | 82.8148 | 2.027 | 0.05299 |
| Palmitic/linolenic | −75.8121 | 44.9913 | −1.685 | 0.10395 |
| Oleic/linoleic | 14.4561 | 7.1449 | 2.023 | 0.05344 |
| Oleic/linolenic | 6.5500 | 7.1294 | 0.919 | 0.36668 |
| Linoleic/linolenic | 107.9349 | 51.2260 | 2.107 | 0.04492 * |
| Palmitic/oleic/linolenic | 9.3591 | 4.1992 | 2.229 | 0.03469 * |
| Palmitic/linoleic/linolenic | −16.0030 | 7.4376 | −2.152 | 0.04089 * |
| Oleic/linoleic/linolenic | −1.4927 | 0.7304 | −2.044 | 0.05123 |

* This model should be refuted due to the high variance inflation factors. **: $p < 0.01$; ***: $p < 0.005$.

Across all models, the value of R^2 was above 0.94. The highest R^2 was observed when omitting either linoleic or linolenic acid. The importance of the interaction terms was highlighted by comparing a model with only main effects (no interactions) with an R^2 of 0.90. Therefore, the interactions—FAMEs influencing each other's effects—made substantial contribution to the oxidation stability. The individual effects of the five FAMEs on the oxidation stability were not additive; the combinations of the FAMEs had non-additive effects.

When looking at the overall behaviour of the saturated versus the unsaturated FAMEs, a confirmation of the results that we found in the literature can be seen in Figure 1. Here, the unsaturated FAMEs display a negative correlation, and thus, show a decrease in the oxidation stability when the concentration increases. The saturated FAMEs show a positive correlation, and thus, show an increase in the oxidation stability when the concentration increases, which is in agreement with most authors [8,10–13]. The figures, however, clearly indicate that the relationships among the mass percentages of the saturated and unsaturated FAs deviate from linearity.

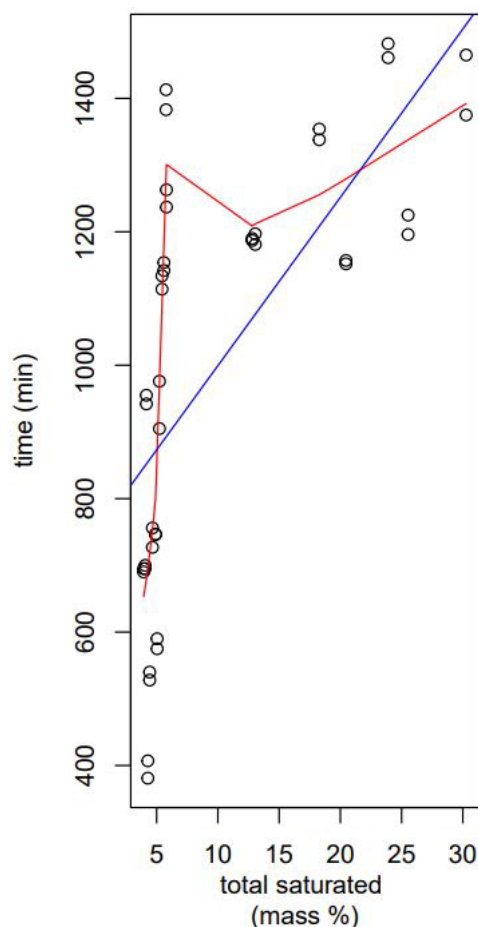


Figure 1. Comparison of the correlation between time and saturated fatty acids. The figure for the total unsaturated mass % versus the time is not shown, as the total saturated and unsaturated mass percentages add up to 100%, and the figure for the unsaturated mass% mirrors the given figure for the saturated mass%. The blue line indicates the linear fit. The red line shows the LOESS trend line.

4. Discussion

The results of this study show that not only do the fatty acids themselves show interaction effects on the oxidation stability but several combinations of two (two-way interaction) and three (three-way interaction) different fatty acids also have a statistically significant influence on the oxidation stability. For one-way interactions, the unsaturation of the fatty acid methyl ester plays a major role, and they are more vulnerable to oxidation. In [10], the number of double bonds is once again mentioned as a major effect on the oxidation stability. The oxidation rate depends on the presence of air and light, which have the most important effects, but also on the presence of metals, which act as a catalyst, peroxides, elevated temperatures, and the size of the surface in contact with air. In [11], the oxidation stability was measured in an air-tight tank without any light. Once more, the degree of saturation was found to make a major contribution to the oxidation stability. With the results obtained, it is in fact clear that the unsaturation plays a major role in the oxidation stability, but in the case of biodiesel, a mixture of FAMES, the interactions among the different fatty acids should also be taken under consideration. According to [12], the oxidative stability strongly depends on the concentrations of linoleate and linolenate, which is indeed what was found in our results (Figures 2 and 3). However, the oxidative stability was not only due to the presence of these FAMES but also due to the interaction of these FAMES with other FAMES.

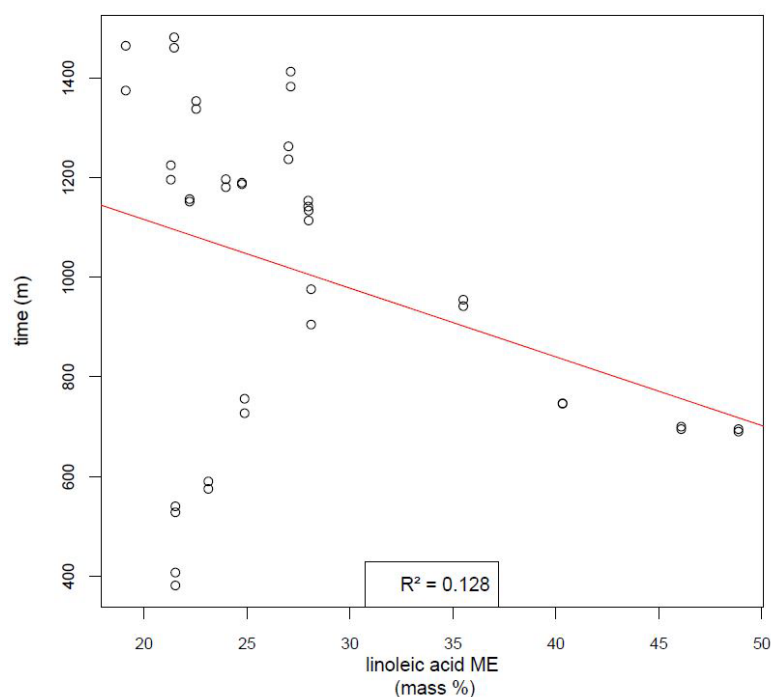


Figure 2. Influence of linoleic acid methyl ester on the oxidative stability. The red line indicates the linear fit.

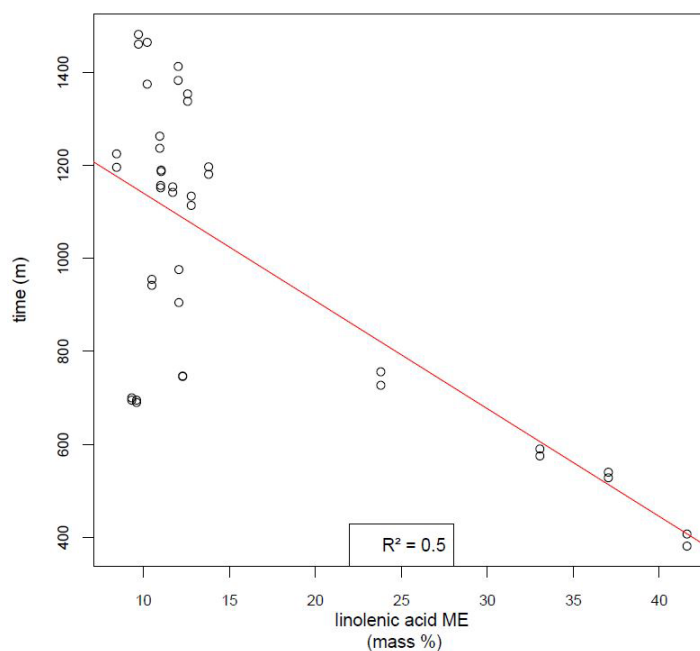


Figure 3. Influence of linolenic acid methyl ester on the oxidative stability. The red line indicates the linear fit.

As the unsaturation in the fatty acid chain portion increased, the biodiesel became more unstable. Can the oxidation stability be improved by taking certain measures? The blending of different types of biodiesels could have a positive effect on the oxidation stability. The more saturated fatty acids the blend has, the better the oxidation stability. Another possibility would be the blending of the biodiesel with mineral diesel, because mineral diesel shows a higher oxidation stability [4]. However, in this case, it should be reminded that the blending of biodiesel with mineral diesel will affect the quality of the exhaust gases, because the exhaust gases will show a higher content of particulate matter,

which should be avoided. When blending biodiesel with mineral diesel, the oxidation stability increases when increasing the concentration of the mineral diesel. The presence of certain antioxidants influences the oxidation stability as well, for example, when the mineral diesel has a lower sulphur content, due to higher refining, the oxidation stability decreases [7]. In [13], a blend of *Jathropa* biodiesel and mineral biodiesel was investigated, and the results showed that a blend of *Jathropa* biodiesel and a 20 volume percent of mineral diesel did not require the addition of antioxidants. Biodiesel was found to be more susceptible to oxidation than vegetable oils [14]. The esterification of the oils is carried out to decrease their viscosity. In the case of maritime transport, the fuel tanks are heated so that the viscosity can be controlled by the heating of the tanks. This means that pure vegetable oils can be considered as fuel, and their oxidation stability becomes less of a problem. Genetically modifying the oil, and thus, the fatty acid composition, could be another solution, as shown in [15]. Genetically modified high oleic sunflower had a higher oxidation stability than regular sunflower oil. These results seemed to be related to the decreased linoleic and linolenic contents in this genetically modified oil. According to [16], the production of biodiesel can also be adjusted to improve the oxidation stability. The transesterification reaction can be catalysed by a homogenous catalyst, such as sodium or potassium hydroxide, in a basic environment or, for example, by sulfuric acid in an acidic environment, or it can be catalysed by a heterogenous catalyst, such as enzymes. The alkali homogenous catalyst seems to be highly hygroscopic, and thus, absorbs more water during storage. After the transesterification reaction, glycerol and alcohol have to be removed from the desired product. This has usually been performed by water washing, but membrane technology shows better results because of the time and energy consumption and improving the quality of the biodiesel.

5. Conclusions

The findings in the literature are focused on the degrees of saturation and unsaturation of the fatty acid composition. Unsaturated FAMES will decrease the oxidation stability, whereas the saturated components will increase the oxidation stability. Different techniques to improve the oxidation stability are used, for example, genetic manipulation, adding antioxidants, blending with mineral diesel, production methods, and so forth. The idea is that we consider B100 because the air quality is our first concern. Therefore, the basic idea is to improve the fatty acid composition by manipulating it in such a way that the oxidation stability is optimal. The oxidation stability is a function of the degree of saturation/unsaturation of the fatty acid composition, but the two- and three-way interactions also play a certain role in the oxidation stability and are statistically significant, so cannot be neglected. This makes the calculation of an optimal fatty acid composition to improve the oxidation stability very complicated. A mathematical/statistical method is not yet available, nor is another experimental method to find the optimal fatty acid composition, and these might be interesting research questions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su151310310/s1>, Figure S1. Influence of the specific fatty acid methyl ester on the oxidation time. Table S1. Statistics of the oxidation times of the different biodiesel blends.

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